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Chemical Stability and Corrosion Division
and
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Center for Materials Science
National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234

March 1980

Annual Report

Prepared for
Federal Highway Administration
Paving and Structural Materials Group
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Abstract

The progress on a research program directed at developing a nondestructive method for measuring the corrosion of steel in concrete as related to bridge deck deterioration is reported. Several polarization techniques for measuring the corrosion rate of steel in concrete are correlated to actual weight loss measured gravimetrically. The design of a prototype automated minicomputer system for measuring the corrosion of steel in concrete is also described. Included are the results of a laboratory basic study on the effect of pH, Cl^-, O_2, and moisture on initiating and maintaining corrosion in mortar.

INTRODUCTION

New technology is being used at an increasing rate in efforts to control corrosion of reinforcing steel in concrete bridge decks. These approaches range from modification of the concrete environment by barrier type road surfacing materials that exclude chemical components necessary for the corrosion to proceed, to protective coatings applied directly to the steel reinforcing bar during its manufacture. Other techniques include impressed current systems which electrochemically modify the reactions at the surface of the steel in concrete thereby reducing its corrosion.

Many of these techniques appear promising. However, there is a need for some method of evaluating the effectiveness of these approaches. It is the purpose of this project to develop a nondestructive field instrument and associated methodology to accurately measure the rate of corrosion of steel in concrete slabs and evaluate its applicability to bridge structures. This capability will allow one to monitor the progress of corrosion as a function of time and bridge deck modifications.

This program is divided into six tasks briefly described in the following.

Task A: This task involves making a literature search to identify the techniques that have been developed for measuring the rate of corrosion of metals, and, in addition, identify commercial equipment available for measuring the corrosion of steel in concrete.

Task B: The two most promising techniques identified in task A are then to be adapted to measuring the corrosion of steel in concrete and evaluated on their applicability.

Task C: On the basis of the information found in task B, one technique is chosen and further tested and developed for application to measuring the corrosion of steel in concrete.

Task D: Define the measuring procedures, and design and build an automated prototype system to permit routine use. Test the prototype on steel in concrete specimens.

Task E: Update the drawings and specifications to permit fabrication of the instrument by a commercial firm.

Task F: Evaluate the applicability of the instrument to measuring the corrosion of reinforcing steel in a bridge deck.

Summary of the Previous Year, Task A: The literature search conducted for Task A resulted in a National Bureau of Standards Special Publication Number 550 titled "A bibliography on the Corrosion and Protection of Steel in Concrete." This document is a bibliographic list of references of published papers, reports, and talks regarding the corrosion of steel in concrete and related subjects. The references are presented in two forms: 1) A subject index divided into six major subheadings including reviews, factors affecting corrosion, measurement techniques, protection techniques, concrete design and related fields, and 2) An author index in alphbetical form. A total of 394 references are listed covering the period from January 1964 to November 1978.

A second document, titled "A Review of Techniques for Measuring the Corrosion of Metals in Concrete" described the methods presently being used to measure the corrosion of metals in an electrolyte. The possible problems and limitations of these techniques when applied to corrosion in concrete were discussed. The use of these techniques in commercially available corrosion measuring devices is also described.

Results During the Past Year

This portion of the report will be divided into three sections. The first section describes the application of several techniques for measuring the corrosion of steel in concrete. The second section discusses the procedure being followed in the development of an automated system for making the corrosion measurement. The third section describes the results of a basic study on the effect of four parameters (pH, O_2, Cl^-, moisture) on the corrosion of steel in three environments, including mortar.

Corrosion Measurement Techniques, Task B: The essence of this portion of the study was reported at the FHWA Research Conference in Williamsburg, VA, December, 1979. That report is attached as Appendix A. Parts of that report will be elaborated upon here along with an update of some of the latest work.

The design of the concrete slab was changed several times through the course of the initial parts of the study. Two considerations were deemed important in the final design. First, it was desirable to simulate the geometric arrangement and the chemical environment of a bridge deck. This resulted in the use of parallel steel bars in a typical bridge deck concrete mix as reported. Second, it was necessary that we be able to weigh our rods for weight loss determinations; the weight and, thus, the size of the rods was determined by the maximum capacity of our analytical balances. The first trial castings were made using standard rebar. After curing, the castings were broken and the rebar removed. It was quickly apparent that complete removal of the concrete would be difficult without damaging the steel bar. It was decided to use a smooth finish bar of low carbon steel instead. This was a benefit for the study

because not only did it make it easier to remove the concrete from the steel, but now the surface area of the steel was clearly defined. In addition, the chemical composition of low carbon steel rod is consistent, unlike the composition of rebar which varies from batch to batch. Three bars were arranged in the slab so that the center rod could serve as a counter electrode. The other two were positioned so that one was close to two outer surfaces of the slab, and the other located so that it was close to only one surface (Appendix Figure 1). In this way more oxygen was available to one than the other.

All of the data reported in Appendix A were obtained on concrete slabs immersed for various periods of time in an aqueous NaCl solution after curing. More recent studies include data taken on slabs to which the chloride is added to the concrete before casting. The measurements of corrosion by polarization methods on these new slabs indicate that the corrosion of the steel is initiated almost immediately after casting as shown in Figure 1. At the same time, the resistivity of the concrete is measured as described in Appendix A. As noted in the earlier work, the corrosion appears to have a strong dependence on the resistivity of the concrete.

On two occasions corrosion measurements were also made on concrete slabs belonging to the Federal Highway Administration (FHWA) and located at their Fairbank Highway Research Station in McLean, VA. These measurements consisted of using Stern-Geary's, Barnartt's, and Mansfeld's techniques. The following table displays the results obtained.

Block	7 September 1979 Stern-Geary	Barnartt	20 September 1979 Stern-Geary	Mansfeld
283	72.3 μA	16.6 μA	14.5 μA	poor least square fit to equation. Not acceptable.
302	325 μA	solution indeterminate	181 μA	Same

Thus, it was found that of the two slabs, block 283 on slab 67-33 exhibited the lowest corrosion current as compared to block 302 on slab 95-17.

In summary of Task B, four polarization techniques have been applied to measuring the corrosion of steel in concrete. These techniques were Stern-Geary's, Schwerdtfeger's, Mansfeld's, and Barnartt's. Compensation of IR was accomplished through use of a modified Holler's bridge circuit. Comparison of weight loss calculated from polarization data to weight loss gravimetrically determined indicated that electrochemical measurements tend to overestimate weight loss by 17% to 86% with the Stern-Geary technique giving the best agreement at 17%.

Refinement of Technique, Task C: Refinement of the polarization technique to improve its suitability to the measurement of corrosion of steel in concrete is the goal of this segment of the study.

The biggest concern remains the determination of current distribution on a bridge deck during polarization measurements. This is of importance because this distribution affects the corrosion current density calculation. In the case of small slabs, this determination is not a problem since the experiment is designed so that the entire surface of the steel bar being measured is polarized. With a bridge deck, however, the structure is so large and complex that it is difficult

and impractical to attempt to polarize all of the steel in the concrete. In fact, if one could limit the area being polarized, then local high corrosion areas could be found if they exist.

Thus, in addition to characterizing the current distribution from a single counter electrode, we are also attempting to develop a counter electrode system that would confine the distribution of current to a known region of the bridge deck. In principle this is done by using a counter electrode having a second counter electrode concentrically located around it. Both would be maintained at the same electric potential with respect to the steel in the concrete, but the driving current to the two electrodes would not come from the same source. The electric field of the outer concentric electrode would confine the current distribution of the inner electrode to a known area. Since the current sources are separate, the polarizing current of the inner electrode, whose current distribution is now known, can be measured.

Up to this point in the study, $Cu/CuSO_4$ reference electrodes at the concrete surface have been used to measure the potential of the steel. This type of reference is very satisfactory where corrosion measurements are made at infrequent intervals of time. At some future time it may be desirable to monitor the corrosion of a bridge deck continuously. For this purpose, a permanently imbedded reference electrode is best.

Several solid reference electrodes are under consideration. These are:

metallic zinc, thallium,

$Cu/CuSO_4 \cdot CaSO_4 \cdot 1/2\ H_2O$

$Zn/ZnCl_2 \cdot CaSO_4 \cdot 1/2\ H_2O$

The electrodes have been made and will be included in the next set of concrete slab specimens.

To summarize Task C, the problem of current distribution is being addressed in two ways. First by characterizing the current distribution from a single counter electrode, or second, by confining a concentric field electrode. The suitability of solid permanent reference electrodes is being investigated. Finally, the polarization measurements are being continued with slabs under various conditions of exposure.

Automated System, Tasks D and E: The ultimate result of this program is to be the design and development of a laboratory system capable of serving as a prototype for an instrument to be used in the field for the measurement of corrosion rates by electrochemical techniques. Much of the work performed on this project will therefore be ultimately utilized in the design philosophy and implementation of the measurement system. By implication, this could be considered to be a valid reason for delay in the development of the instrument. However, there already exists an array of information sufficient to establish basic criteria for the initial design.

At this stage, it is worth noting that all existing methods for the measurement of corrosion rates by electrochemical techniques, ultimately devolve to a measurement of voltages (AC or DC) proportional to either corrosion current or potential. Thus, it is apparent that any technique used in the final system requires a means of determining potential in a precise manner. A flexible means of choosing the source to be measured is also required.

Any system to be used for the routine measurement of a physical quantity must of necessity be capable of operation in a non-complicated fashion. Operator skills vary and complexities in the experiment should be limited to the setup of the cell, in order to minimize the necessary training. In principle, once connected, the measurement should involve only a "Start" signal, with all other aspects of the experiment controlled by the equipment itself. However, provision must be made for changes in the experimental technique used, in order to suit either varying conditions or as a result of the ongoing work in the other portions of this project. As already discussed, easy access to a variety of voltage sources and a precision voltage measurement method must also be part of the instrument.

Data output must be reliable, relatively noise-free, and capable of permanent storage. Provision must be made for data acquisition over extended periods of time which may imply large quantities of data. The capability of, at least, initial data reduction should be included. Of potential interest would be the capability of transmitting the accumulated data, at fixed intervals, to a remote control site.

Another important consideration, is that the ultimate prototype must be capable of redesign for field use, with a miniumum of effort. This implies that all semiconductors used (discrete devices or integrated circuit) should have militarized (wide temperature range) equivalents, and also that the circuit boards shall be capable of reconstruction in a minimum volume and weight configuration. In addition, circuitry should be low power in order to extend battery life in the field version.

Excluding consideration of the cell, the above discussion provides enough guidelines to design an instrument. This system will be capable of handling almost any type of cell that might be used for measurement.

The first aspect of the problem that must be addressed is the decision as to whether the system should be digital or analog in design. Analog systems have great flexibility, but in general, are not capable of changes without intervention by a skilled operator. Analog data outputs are more susceptible to noise, and as regards permanent storage, are more difficult to save without some kind of analog to digital conversion. Data reduction to a more usable form is generally more difficult. On the other hand, digital systems overcome the data output and reduction difficulties and are essentially as flexible as an all analog system. Where analog systems have a distinct advantage is the greater sensitivity possible and the fact that they can take the data continuously. Even these factors can be handled by a properly designed digital system. An analog "front end" can be used for sensitivity when required, and data can be taken at rates fast enough to emulate the continuous characteristic of analog detection. For these reasons, we have decided to utilize a digital system.

Although the detailed design has only been started, we can outline the basic system (Figure 2). Overall control of the system resides in the CPU (Central Processing Unit), which will be a unit based on an MC6800 type microprocessor. The CPU will contain an ROM (read only memory) and all the utility programs needed to operate each of the other components of the system as well as to perform data manipulations. Also included on the CPU printed circuit board will be generally needed

peripherals such as serial communication interfaces, a "Real-Time Clock," power failure detection and handling, and I/O interfacing to the control-Display panel.

The specific program to be performed (which utilizes the utility programs on the CPU board, as subroutines) will be contained on a PROM (Programmable Read Only Memory) which will be installed by the operator when the unit is to be activated. This PROM will be programmed to direct the instrument through the experiment, according to the technique determined to be useful under the prevailing conditions. Thus, operation of the system would be simplified since the operator would only have to insert the PROM, turn the unit on, enter any needed parameters, as requested by the program, and then push a start button. (This assumes connection of the cell has been performed prior to system activation.) The PROM could be replaced by a prerecorded tape. In this case, the operator would load the tape into the system and then perform the other operations. This procedure, however, has a major disadvantage. With this technique, the program would reside in RAM ("Random Access" memory = read-write memory), Power failure, or a burst of excessive noise could ruin the program, whereas a PROM program would be undisturbed except for catastrophic failure of the system.

The "Display-control" panel would be used by the operator on start-up. The display portion would request needed parameters during start-up, which would be entered via the controls. When the start procedure is completed, the CPU would disable the panel except for the power switch. It is worth noting here that these parameters are to be saved in a small RAM that would be saved, in the event of power failure, due to a backup power supply.

The RAM Board would contain a sufficient read-write memory for all temporary data storage. We expect to transfer the results of each reading onto tape as soon as the data reduction is completed. Thus in the event of failure, minimum data loss would occur. Since this also reduces the memory requirement, it also reduces needed power.

The tape recorder and the modem are the data output ports for the system. Each can be used individually, or they can be used in tandem. Upon completion of data reduction, the quantities computed (and/or the raw data) can be recorded on an incremental tape recorder. If a telephone hookup is available, the data could be transmitted from the remote site via the modem to a central facility.

The Converter Board will consist of at least one Digital to Analog converter (DAC) and one Analog to Digital Converter (ADC) with associated controls, amplifiers, etc. The desired resolution and speed will be determined in the course of this study. Inputs to and outputs from the converter board will go to or come from the "Front End" board (analog), or the data bus (digital).

The "Front End" board is not capable of full definition at the present time. Design of this board is technique dependent. If DC methods are used, the front end would essentially be a small potentiostat (LO noise, capable of galvanostatic operation, small signal). If the AC impedance techniques are used, the front end will be different.

All circuitry will be designed utilizing circuits that can be replaced by either Low Power devices or CMOS circuits. Every attempt will be made to ensure that wide-temperature range devices are available as replacements for the prototype semiconductors. In addition, the

possibility of entering a power down mode between measurements will be examined. Either or both of these adaptations would be needed when field models of the prototype are built.

Basic Studies: The literature search revealed that the information on the corrosion of steel in concrete was heavily concentrated on the effects of chloride salts. However, there was little information on the effects of oxygen, pH, and moisture. In fact, no studies on the corrosion of steel in an alkaline environment were found. The first stages of this work sought to develop an understanding of the effects of oxygen, pH, and chloride concentrations on the corrosion of steel. On a more practical level, this information was needed to enable us to control the corrosion process during the development of the corrosion measuring techniques.

Three environments have been used in this phase of the study. The first was an alkaline solution of $Ca(OH)_2$. The second was a wet sand-salt mixture, and the last was mortar. Steel specimens were cut from 1 mm sheet to approximately 2 x 10 cm.

Flat steel specimens were placed in a $Ca(OH)_2$ solution in which the oxygen content was controlled by bubbling an oxygen-nitrogen mixture through the solution in which the pH and chloride content were also controlled. The results indicated that pH controlled the corrosion initiation time as shown in Figure 3. Notice that at a pH of 10.5, corrosion started immediately on immersion. As the pH was raised to 11.5 and 12, about 200 hrs. passed before corrosion started. At a pH of 12.5, in the saturated $Ca(OH)_2$ solution, corrosion of the steel did not occur during the experiment. These results developed in an oxygen saturated environment (8 ppm) in the absence of chloride. With chloride,

the results are essentially the same except that the initiation time to corrosion was reduced as shown in Figure 4, but again, no corrosion occurred in the high pH saturated solution of $Ca(OH)_2$. It is of interest to note that in these oxygen saturated solutions, once initiated, the corrosion rate (slope of the curves) was constant irregardless of pH or chloride content. Not surprisingly, however, the oxygen content of the solution had a large effect on the corrosion rate of steel as shown in Figure 5. As before, corrosion did not develop in the high pH of a $Ca(OH)_2$ saturated solution at any level of oxygen. The results clearly show that oxygen controls the corrosion rate, pH controls the initiation time which is also somewhat affected by chloride content.

The interaction of oxygen, pH, and chloride is more complex and in combination can develop conditions that lead to corrosion of steel even in saturated $Ca(OH)_2$ solutions. Figure 6 is a summary of these data showing these three parameters. The surface developed by these parameters is a boundary within which corrosion does not occur. Outside of this boundary, corrosion of steel has been observed. For example, where it was shown earlier that chloride or oxygen acting alone could not cause corrosion of steel at a pH of 12.5, this figure shows that at an oxygen concentration as low as 2 ppm and at a Cl^- concentration of 8 mol/l, corrosion does occur, and can also develop at lower concentrations of chloride at higher oxygen contents. This figure will be referred to again.

To observe the effect of moisture on the corrosion of steel, specimens were imbedded in a mixture of sand, $Ca(OH)_2$, and NaCl. The mixture was held in small perforated crucibles in an atmosphere of flowing air saturated with moisture. This configuration allowed the specimens

to be removed for weight loss determination during the course of the experiment. These specimens were initially exposed to two conditions of moisture. In the first condition, specimens were imbedded in a dry sand mixture, and the second condition consisted of specimens imbedded in a moisture saturated sand mixture. Figure 7 illustrates the response of the corrosion as a function of time. Specimens placed in the saturated sand mixture did not corrode, but during the same period, the specimens in the dry mixture began to corrode almost immediately as moisture was introduced. The corrosion rate of these specimens decreased steadily as the moisture content of the sand mixture increased; and at saturation, the corrosion rate ceased. When these same specimens were transferred to a dry air environment, the corrosion rate began to increase again as shown in the figure. Thus, the degree of moisture plays a very important role as expected; however, the cessation of corrosion at saturation was not anticipated.

After the initial studies in sand mixtures and solutions, the work was extended to include steel in mortar. Steel specimens were cast with a 5 mm cover of mortar containing chloride. After 24 hours, half of the specimens were immersed in a $Ca(OH)_2$-NaCl solution, and the other half were allowed to dry for one week before immersion. The corrosion current of each specimen was evaluated by polarizing the specimen from -10 to 10 mv with a potentiostat and plotting the overvoltage as a function of the polarizing current. Figure 8 illustrates the type of data that resulted. The slope of this curve is inversely proportional to the corrosion rate of the steel in mortar. As in the case of the sand mixture, the corrosion of the steel in mortar that was kept continuously wet was near zero as illustrated in Figure 9. The specimens that were allowed to dry for one

week and then were immersed, initially developed a high corrosion rate that decreased with time to a very low value.

On the basis of the O_2, pH, Cl^- diagram shown in Figure 10, the corrosion observed in mortar can be explained. The pH of the mortar after casting is very high and of the order of 12.5, and the concentrations of Cl^- and O_2 are well within the region of no corrosion. However, as the concrete cures and dries, the chloride becomes more concentrated. At the same time this moisture loss allows an increase of oxygen diffusion through the mortar leading to the development of conditions that move the concrete into the corrosion region of Figure 10 (dashed line). Once corrosion is initiated by this process, the pH is forced to decrease at the anode by the reaction:

$$Fe^{++} + 2\ H_2O \rightarrow Fe(OH)_2 + 2\ H^+$$

These concentration cells are very small and act over a short distance because of the increasing resistivity of the concrete. Once this initial phase takes place and the pH is reduced locally, then corrosion proceeds more easily.

In summary, the basic study has shown that at low concentrations of O_2 and Cl^-, pH controls the initiation of corrosion. But as O_2 and Cl^- increase, they cause a reduction of pH at the anodic areas. In concrete, it is hypothesised that Cl^- and O_2 can increase at the steel surface during drying of the concrete to sufficiently high values to initiate corrosion. This corrosion process reduces the pH of the concrete at the anodic areas of the steel and makes it easier to initiate corrosion in future times when moisture and O_2 are available.

Plans for this Coming Year

The techniques of applying a polarizing potential to a steel specimen and the measurement of the resulting signals will continue to be improved.

This will include increasing our knowledge of the distribution of current from a single counter electrode, or developing a system of concentric electrodes to confine the current to a known area.

An evaluation of various permanent reference electrodes to determine their stability over several months of use in different conditions of concrete will also be carried out.

A prototype automated system for measuring the corrosion of steel in concrete will be assembled and tested in the laboratory. On the basis of this, the design will be updated for fabrication by an outside firm. Task F will evaluate the applicability of the instrument for measuring the corrosion of steel in a bridge deck.

The basic study will be continued with an emphasis at applying what has been learned to the development of a new technique for measuring the corrosion of steel in concrete.

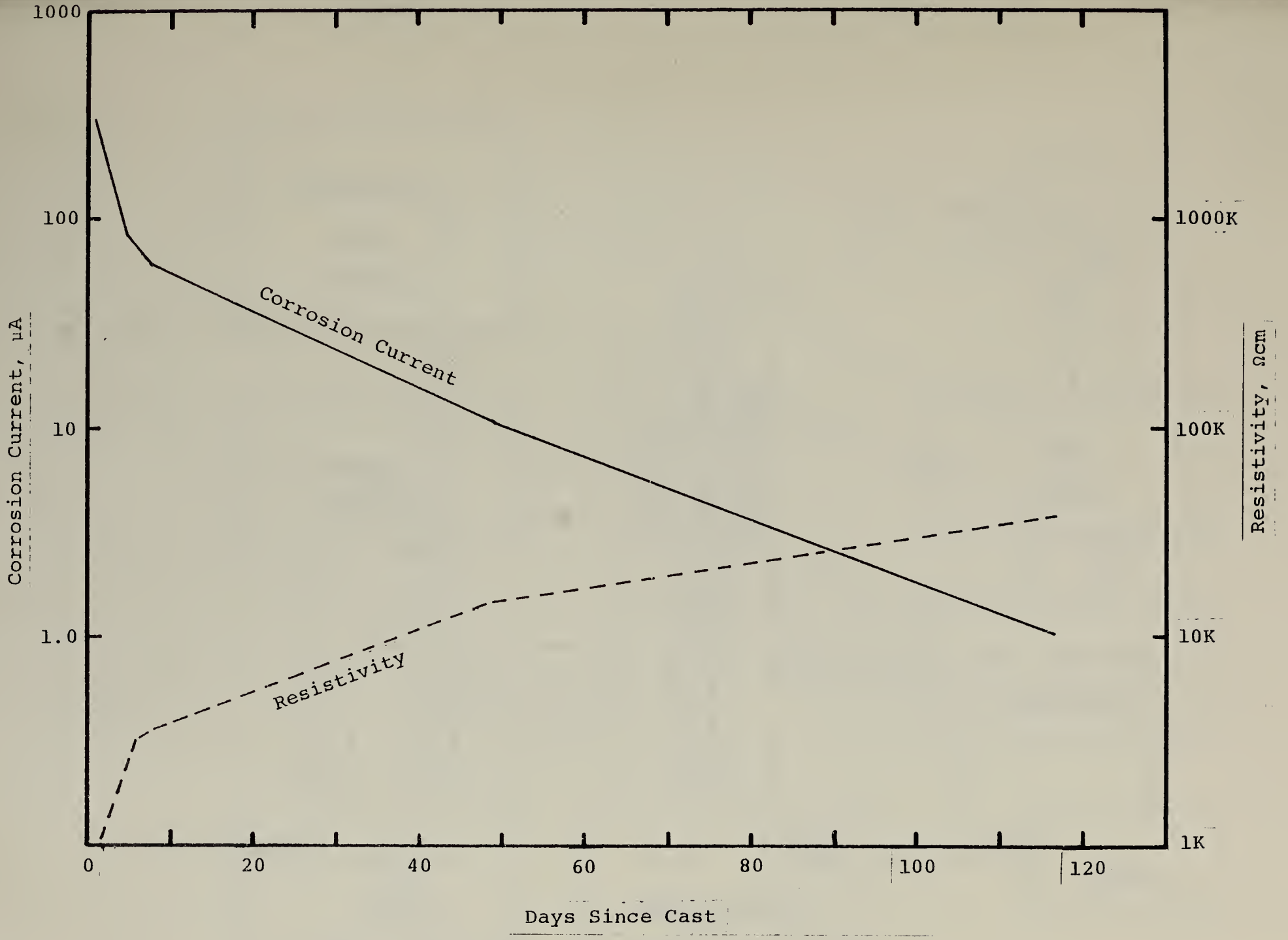

FIGURE 1. Corrosion Current and Resistivity Versus Time

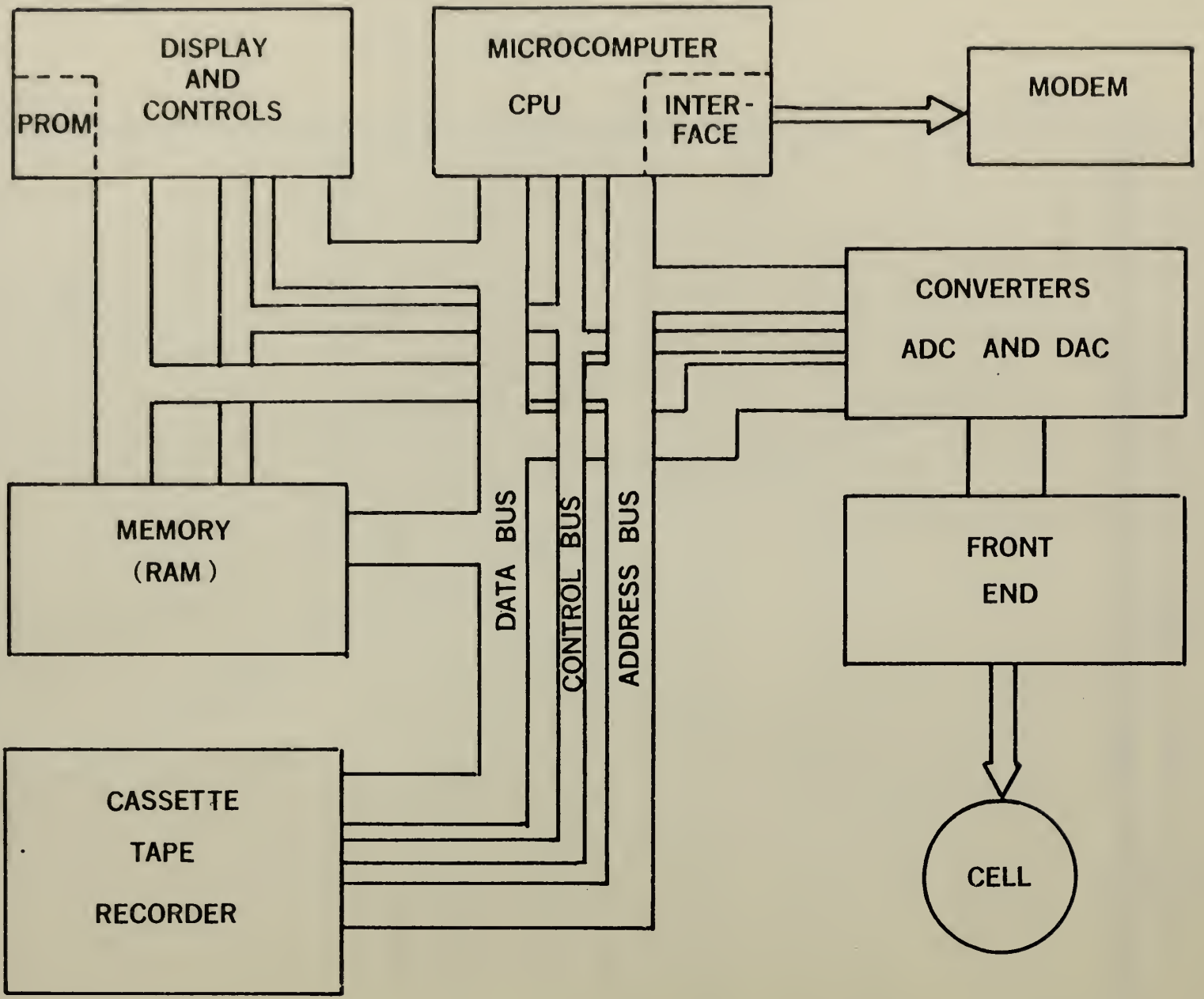

FIGURE 2. Block Diagram Illustrating Design of Automated System

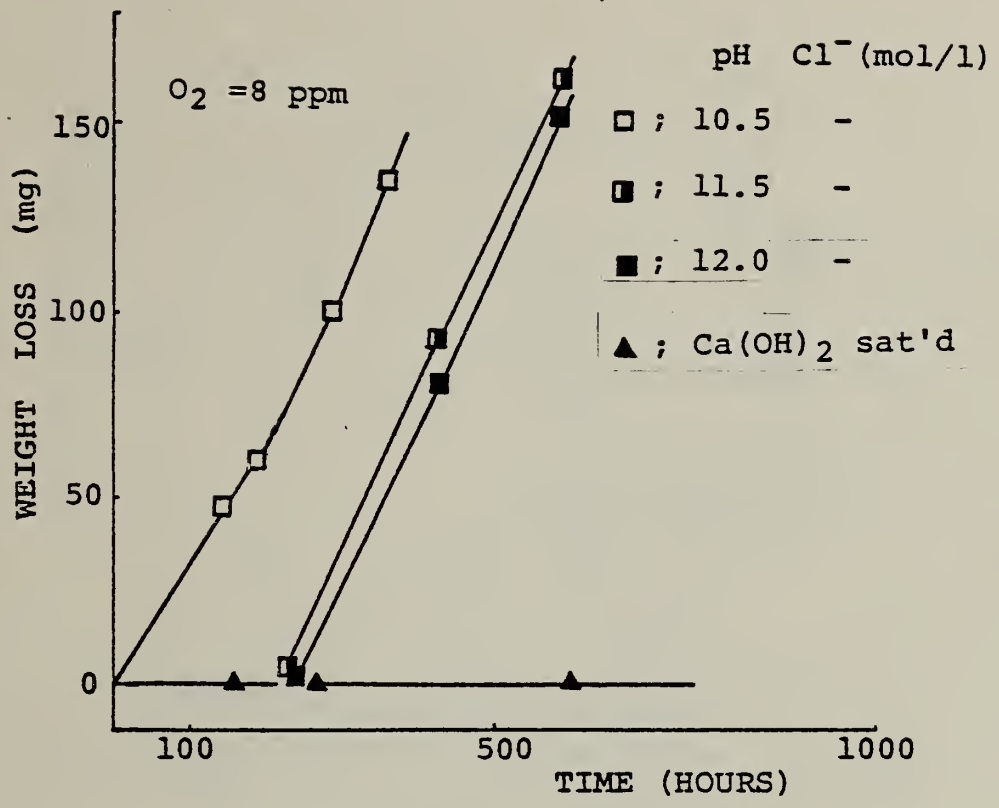

Figure 3. The Effect of pH on the Corrosion of Steel in the Absence of Chloride

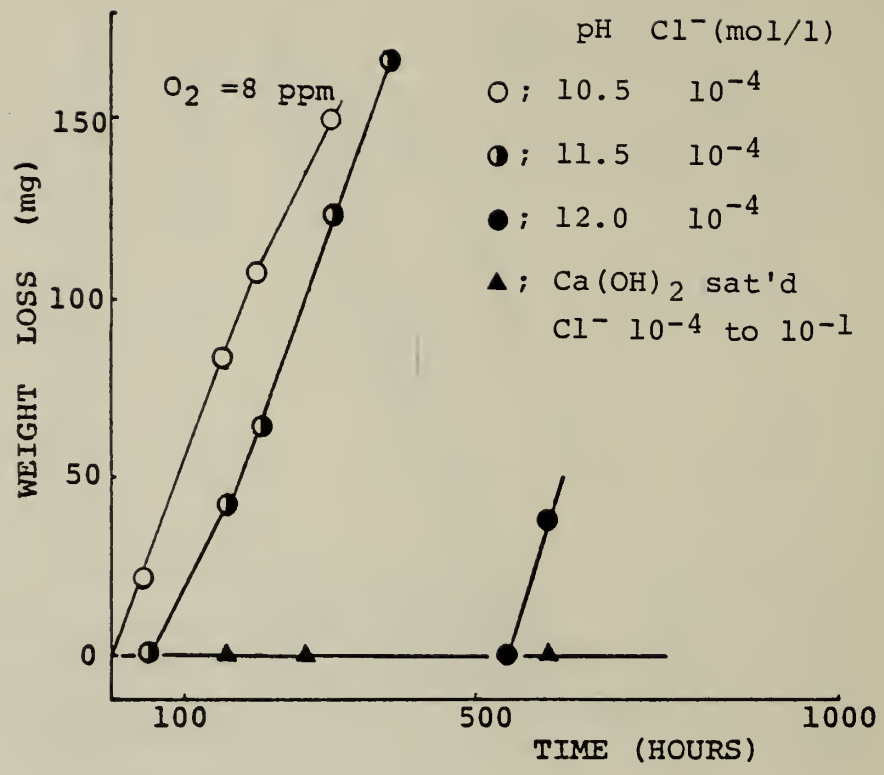

FIGURE 4. The Effect of pH on the Corrosion of Steel in the Presence of Chloride

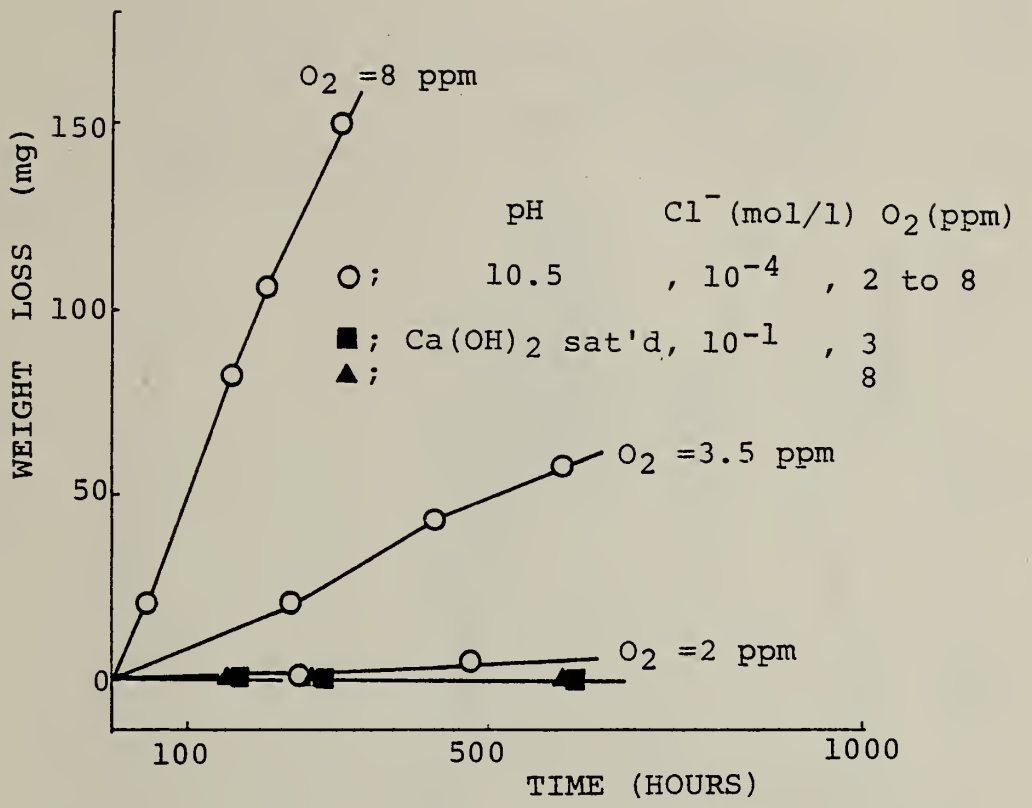

FIGURE 5. The Effect of Oxygen on the Corrosion of Steel

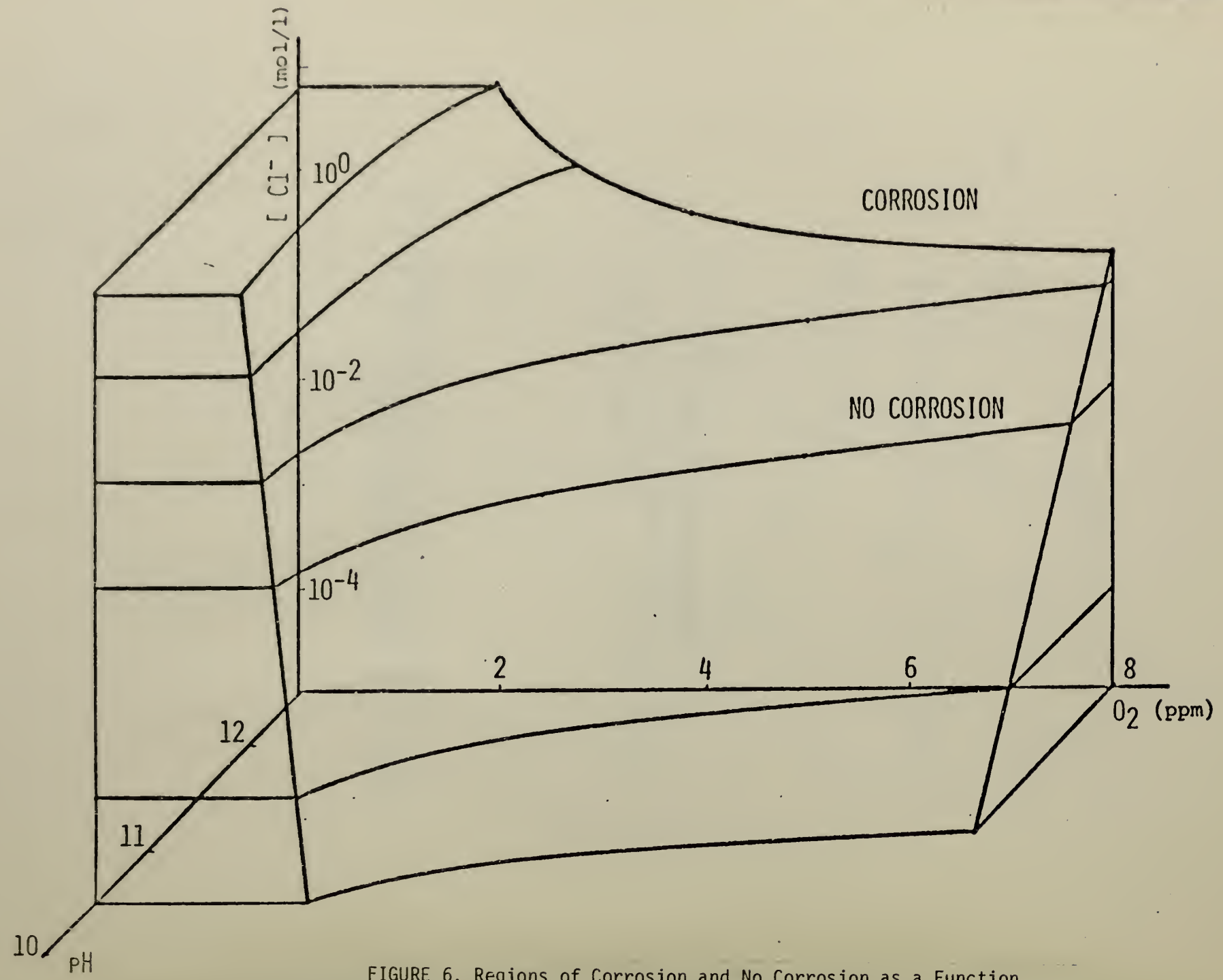

FIGURE 6. Regions of Corrosion and No Corrosion as a Function of pH, Chloride Concentration, and Oxygen Concentration

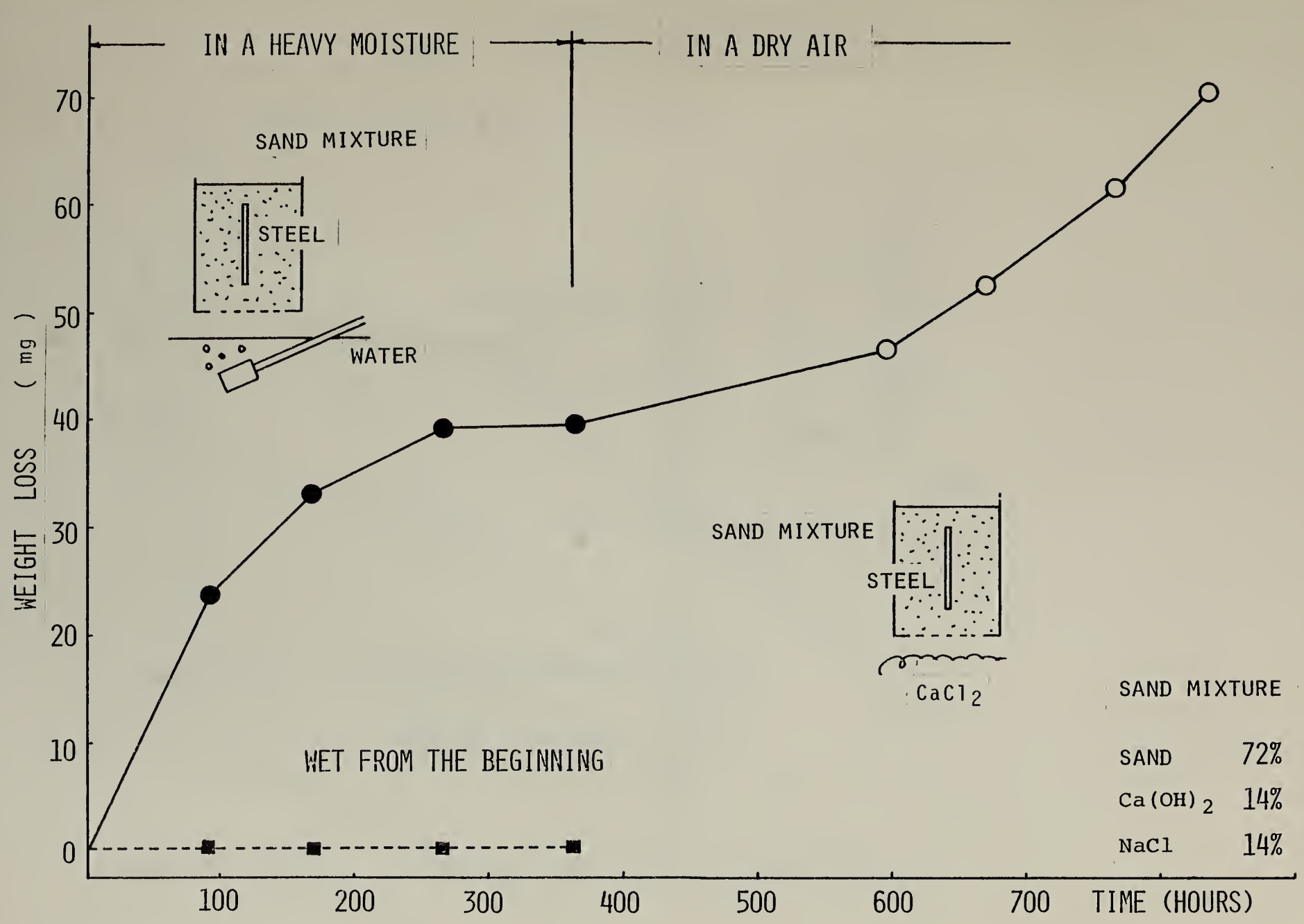

FIGURE 7. The Effect of Moisture on the Corrosion of Steel in a Sand, $Ca(OH)_2$, NaCl mixture

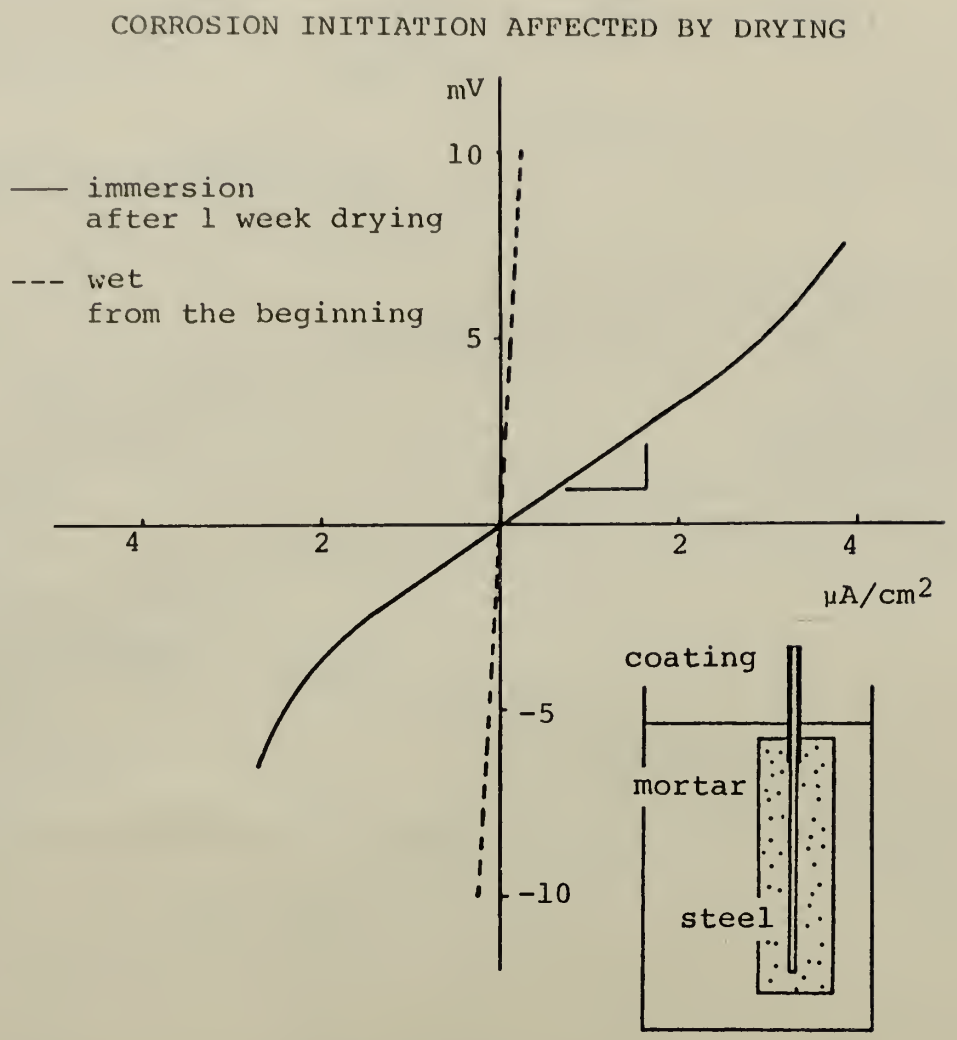

FIGURE 8. The Effect of Degree of Corrosion of Steel on the Slope of the Polarization Curve

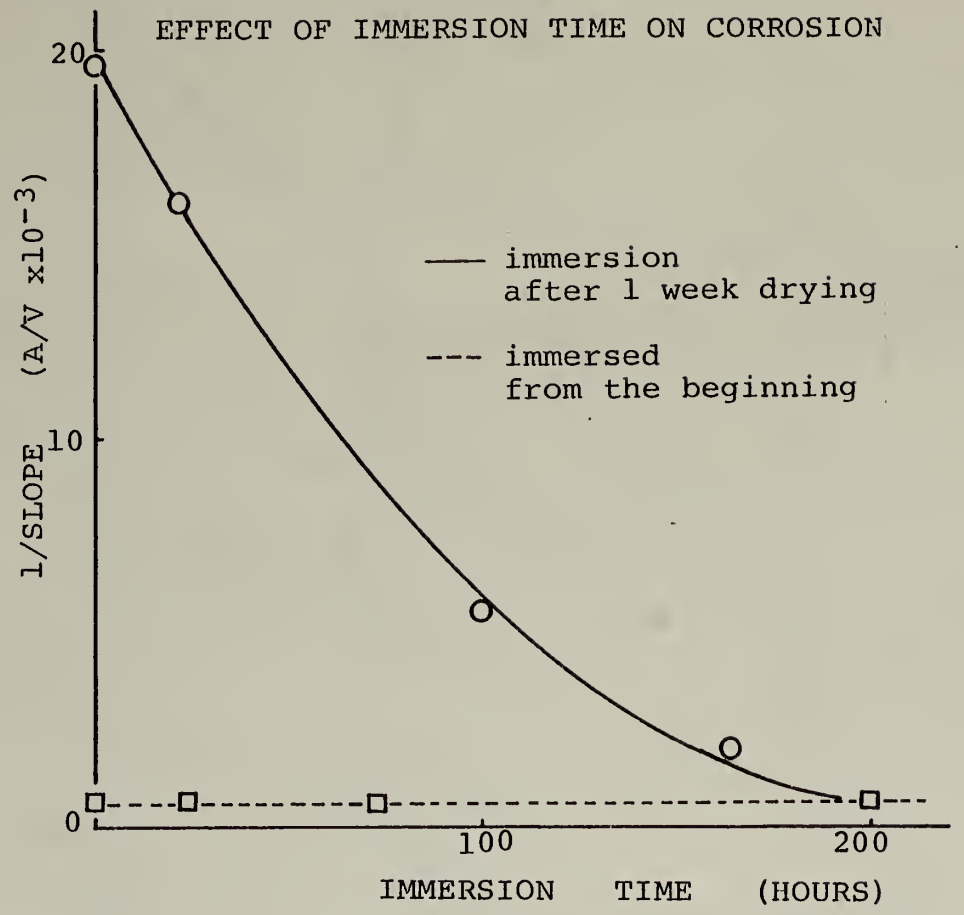

FIGURE 9. The effect of Oxygen Depletion Resulting From Immersion on the Corrosion of Steel as a Function of Time

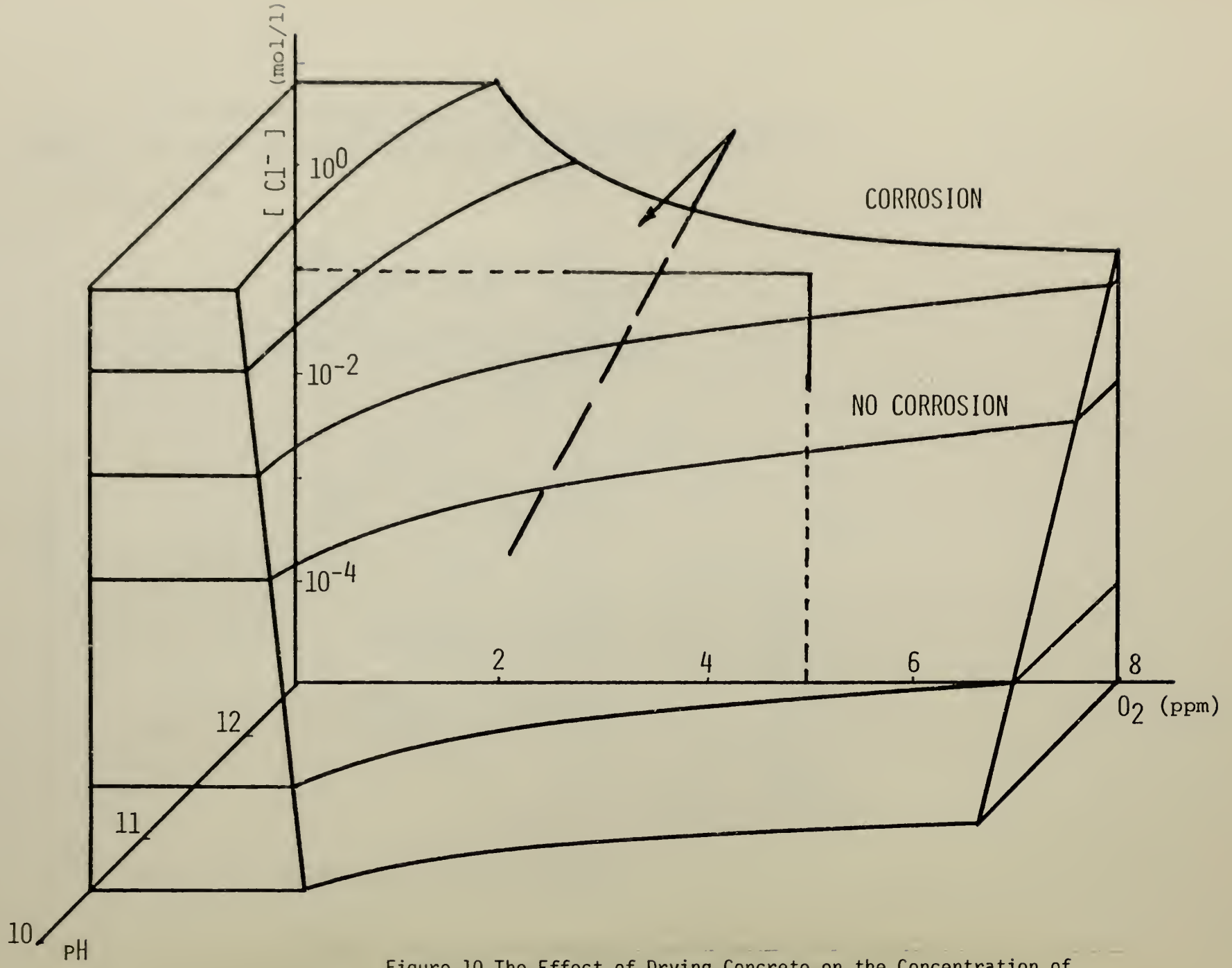

Figure 10 The Effect of Drying Concrete on the Concentration of Chloride and Oxygen

APPENDIX A

MEASURING THE CORROSION RATE OF STEEL IN CONCRETE

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The corrosion of steel in concrete where deicing salts are used has become a serious problem in the United States. The corrosion of steel is particularly insidious in that generally the extent of corrosion is not evident until damage to the structure is sufficiently severe that remedial measures are necessary. There is a need for the development of some process whereby the progress of corrosion deterioration can be evaluated at its initial stages before external damage appears.

An earlier study of the literature revealed that much of the work reported has been concentrated on the effect of chloride while considerably less work has been done on the effect of pH, oxygen, and moisture (1). The study also revealed that the most widely accepted method for detecting corrosion in concrete is Stratfull's technique of mapping the half cell potential of steel from the surface of the concrete (2). This approach, however, does not reveal information on the rate of deterioration. Dawson has shown that the a.c. impedence technique is useful in measuring the rate of corrosion of steel in alkaline solutions and concrete slurries in a laboratory setting, but evaluation of the data becomes difficult when applied to steel in concrete (3).

It is the purpose of this paper to set forth one approach to the solution of this question. Presently, studies are being carried out at the National Bureau of Standards where the factors affecting the corrosion of steel in concrete are being investigated and an electrochemical technique for measuring the corrosion rate of steel in this environment is being developed.

*Research Associate, Nippon Steel Co., Japan

Materials and Procedure

Steel specimens for this study were made from 1.27 cm diameter AISI 1017 steel rod 55 cm long. Pretreatment of the rods consisted of immersion in a 50% solution of HNO_3, rinsing in water, followed by immersion in a saturated solution of $Ca(OH)_2$ for 2 hours. Specimens were rinsed again and dried in preparation for weighing with an analytical 2 Kg capacity beam balance having a sensitivity of $\pm$0.5 mg.

Figure 1 illustrates the concrete slab and the placement of the three specimens within the casting. The composition ratio of the concrete was 1 part cement, 0.5 parts water, 1.9 parts sand, and 3.4 parts pea gravel. After casting, the concrete was vibrated and covered with a plastic sheet during initial curing.

After several days of curing, the concrete surface from which the steel specimens exit from the concrete was coated with a silicone base rubber to reduce the corrosion effects at that interface. More recent slabs are being coated with beeswax. The resistivity probes also shown in the illustration are two 3 mm diameter type 304 stainless steel rods each 6 cm long. The probes are placed in the concrete during casting, and are 2 cm apart center to center and imbedded 4 cm. Calibration of this configuration of rods using a 120 Hz signal indicates that the resistance reading between the two rods multiplied by a factor of approximately 5.1 is the resistivity of the system in Ωcm. The resistivity of all recent slabe is determined each time a corrosion rate measurement is made. Three conditions of treatment of the slabs will be described here. The first condition of exposure was to simply allow the slab to remain in laboratory air having a relative humidity of approximately 30% with an air temperature of 22°C. The second condition of exposure was to cure the concrete for 29 days, then immerse the slab into a saturated solution of NaCl for six days, and then allow it to remain in laboratory air. The third condition of exposure was to allow curing to proceed for 50 days, then immerse the slab in a 3.5% solution of NaCl for 24 hours, and

follow this with daily ponding (wetting) of the slab during week days with a 3.5% NaCl solution. This ponding was stopped after 40 days.

Removal of the specimens from the concrete after exposure consists of breaking away the concrete from the specimen using a 1 Kg hammer. Practically all of the concrete is removed in this way. The final small residue remaining is removed by lightly tapping with the side of 1 cm diameter steel rod approximately 10 cm long. Final cleaning is done with a plastic scouring pad. Thin stubborn films of oxide are not removed. However, where active corrosion is taking place and pitting has occured, the surface is easily cleaned in the manner described. A satisfactory chemical cleaning procedure has not been found. The specimens are weighed for weight loss determination.

Polarization Measurements

The determination of corrosion rate from polarization data is based on the observation that the current necessary to change the corrosion potential of a metal is directly related to the rate of corrosion of the metal in the electrolyte. The techniques differ only in how this change in potential is achieved. Four techniques of polarization have been used in this study, however, most of the data has been obtained through Stern and Geary's method.

Stern and Geary consider the slope of the overpotential, ΔE, of the specimen versus the applied current, I, for small values of overpotential (4). This slope is related to the corrosion current, I_{corr}, by their relationship:

$$\left(\frac{dE}{dI}\right)_{E \to o} = \frac{b_a b_c}{2.3(b_a + b_c) I_{corr}}$$

where b_a and b_c are the anodic and cathodic Tafel slopes respectively. For calculation of the corrosion current, I_{corr}, values for the Tafel slopes must be obtained from other sources.

In this case the overpotential used has been 6 mv and the assumption made that $b_a = b_c = 100$ mv.
Thus:

$$I_{corr} = 21.7 \frac{I}{\Delta E_{mv}} .$$

The second technique used is Schwerdtfeger's empirical determination of the corrosion current, I_{corr}, from the change in slope of the polarization curve (5). The cathodic corrosion current, Ip, and the anodic corrosion current, Iq, are found at this "break" in the curve, and the corrosion current is then calculated from:

$$I_{corr} = \frac{I_p \cdot I_q}{I_p + I_q}.$$

The technique requires that the polarization curve cover an overpotential of $\pm$ 100 mv so that the "breaks" in the polarization curve may be observed.

The three point method of Barnartt is the third technique that has been used (6). Three overvoltage/current data points are measured along the polarization curve, and from this b_a, b_c, and I_{corr} are calculated. If the first overpotential point is at ΔE, then the second and third are at $2\Delta E$ and $-2\Delta E$ respectively. The resulting currents at each potential are measured and substituted into the ratios

$$r_1 = I_{2\Delta E} / I_{-2\Delta E}$$

and

$$r_2 = I_{2\Delta E} / I_{\Delta E}$$

which in turn are related to each other through the quadratic equation

$$U^2 - r_2 U + \sqrt{r_1} = 0.$$

The solution of this equation yields the relations that allow one to solve for the Tafel slopes b_a and b_c. Using the relationship of I/I_{corr} versus ΔE, the corrosion current for the process is found.

The fourth technique is a computer analysis of polarization

data developed by Mansfeld (7). The computer makes a best fit analysis to theoretical curves generated for different values of Tafel slopes and in this way b_a, b_c, and I_{corr} are found.

The polarization techniques described employ a three electrode system having one electrode as the steel specimen under study, a second electrode serving as a voltage reference, and a third electrode from which current is impressed on the specimen. The type of reference electrode used in this study is the $Cu\text{-}CuSO_4$ electrode. Contact is made to the concrete slab through a small wetted sponge located at the concrete surface directly above the steel specimen being polarized. Where the concrete is chloride free, the sponge is wet with a saturated solution of $Ca(OH)_2$. If chloride is present in the concrete then a 3.5% NaCL solution is used to moisten the sponge. In all cases the sponge is firmly squeezed to remove excess solution which may affect the moisture content of the concrete. Generally, the counter electrode, the electrode from which current is impressed on the specimen, is the center rod of the three rods in the slab. Corrosion measurements are made on the outer two rods, but not simultaneously.

The circuit used for polarization measurements is Holler's (8) which incorporates a Wheatstone bridge for IR compensation as illustrated in Figure 2. The IR compensating design takes advantage of the fact that when an external polarizing current is applied to a specimen, its rate of change in potential due to polarization is very small as compared to the potential change due to IR. By repeated applications of current of short duration, and by increasing the Wheatstone balancing resistance, the IR component can be compensated as illustrated in Figure 3. Once this balance is achieved, then the polarizing potential free of IR can be measured for all values of applied current. Since the resistance of the concrete changes from day to day, this process of IR compensation must be repeated each time that polarization measurements are made.

Results and Discussions

Before a measurement technique for corrosion could be considered, it was necessary that we be able to cause the corrosion of steel in concrete at will. This proved to be a temporary obstacle until a better understanding of the corrosion process developed. This portion of the investigation will not be discussed here. However, it was determined that for corrosion of steel to be initiated in chloride contaminated concrete, it is necessary that the system go through a drying cycle. It is hypothesised that during this period of moisture loss the chloride is locally concentrated to high levels perhaps approaching saturation. At the same time oxygen becomes more easily available at the steel surface as the porous concrete loses moisture. The micro cells that develop at the concrete/steel interface lead to an increased rate of passive film break down, a local reduction in pH, and subsequently, a sustained corrosion process. The increasing resistivity of the concrete limits the action of the micro cells to short distances of probably less than 1 mm. Eventually, the rising resistivity stifles the corrosion process. Thereafter, any action that reduces the concrete resistivity and improves aeration causes an increase in corrosion of the steel.

The first condition of exposure was a chloride free concrete in laboratory air. The data on two slabs indicates that the corrosion current of the imbedded steel ranged from 2 to 0.25μA over a period of 210 days, and is equivalent to a total corrosion loss of less than 3 mg over the exposure time. Since the surface area of steel exposed to the concrete is 200 cm^2, the calculated corrosion rate is very low at less than 0.007 $mg/dm^2.d$. Visual inspection of steel specimens removed from one of the slabs verifies the excellent condition of the steel surface and the absence of any visible corrosion. Weight loss measurements were considered unnecessary on these specimens.

In the case where the concrete slab was immersed for six days in a saturated solution of NaCL after curing, the second condition of exposure, the corrosion current increased by over an

order of magnitude as shown in Figure 4. After three days immersion, the data indicates that the corrosion rate continued to increase. By the forth and fifth days, the corrosion rate reached a maximum and began to decrease. On removal from the solution, the corrosion rate of the steel decreased gradually. Shown on the same figure is the resistivity of the concrete as measured with the permanently imbedded probes. In a manner similar to the corrosion rate, the resistivity decreased to a minimum value after four to five days immersion and then gradually increased. After removal from the solution the resistivity continued to increase as shown. Clearly the effect of immersion on the corrosion rate was much greater than its effect on the resistivity of the concrete. During drying, however, the resistivity appears to be having a direct influence on the degree of corrosion observed. The corrosion measured on this chloride contaminated slab is over an order of magnitude greater than the corrosion observed in the chloride free environment. Weight loss measurements will not be made on this slab until the data indicates that a measurable amount of steel has been lost.

The third condition of exposure was a 24 hour immersion of a slab in 3.5% NaCL solution, after curing, followed by daily wetting of the slab on weekdays for a period of approximately 40 days. Figure 5 illustrates the response of the corrosion of steel to this treatment. Measurements were not made during the first stages after casting, but based on the corrosion observed on other slabs, it can be assumed that the corrosion current prior to immersion was of the order of 1μA. After the wetting cycles were stopped, the corrosion of the steel decreased slowly as shown. Resistivity measurements were not made on this slab. The calculation of weight loss from the electrochemical data is based on the corrosion current versus time data of Figure 5 and Faraday's equation (9). Total metal loss was calculated to be 172 mg for specimen B in slab number 1. The actual weight loss measured gravimetrically was 147 mg. The average corrosion rate is calculated to be 0.33 $g/dm^2.d$. Visual examination of the steel rod after

removal revealed that the corrosion was confined to three areas on the steel surface, and was in the form of broad shallow pitting. The good agreement between the electrochemically measured and the gravimetrically determined weight loss of steel indicates that electrochemical polarization techniques can be used to measure the corrosion of steel in concrete.

A comparison of the data from the four electrochemical techniques described indicates that all the methods overestimated the weight loss of metal. The Stern-Geary method overestimated the weight loss by 17% while Schwerdtfeger's, Mansfeld's, and Barnartt's techniques overestimated the corrosion by 40%, 56%, and 86% respectively. Since the differences in corrosion rates between a corroding and noncorroding system are over an order of magnitude, then even the data with an 86% overestimation of corrosion may be acceptable.

Summary

The corrosion rate of steel in concrete has been measured using polarization techniques with IR compensation. The four methods used were Stern-Geary's, Schwerdtfeger's, Mansfeld's, and Barnartt's techniques.

The data indicate that the corrosion of steel in chloride free concrete is negligible and less than 0.007 $mg/dm^2 \cdot d$ while in chloride contaminated concrete the average corrosion rate of steel is well over an order of magnitude greater at 0.33 $mg/dm^2 \cdot d$.

Comparison of the weight loss calculated from the polarization data to the weight loss gravimetrically determined indicates that the electrochemical measurements overestimate weight loss by 17% to 86%. However, even with an overestimation of 86% the technique will differentiate between a corroding and noncorroding condition of steel in concrete.

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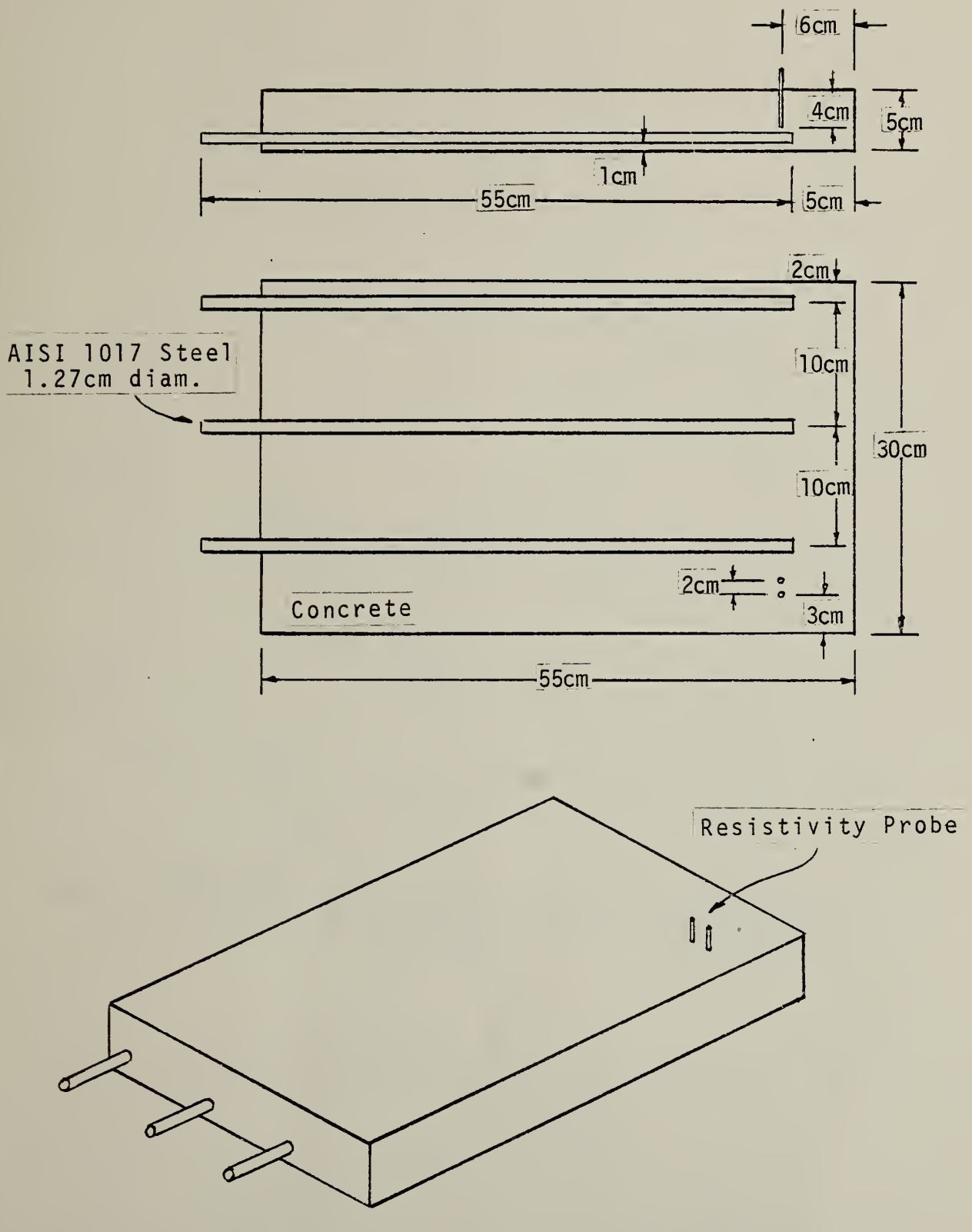

Figure 1. Concrete Slab With Three Steel Specimens And Resistivity Probe

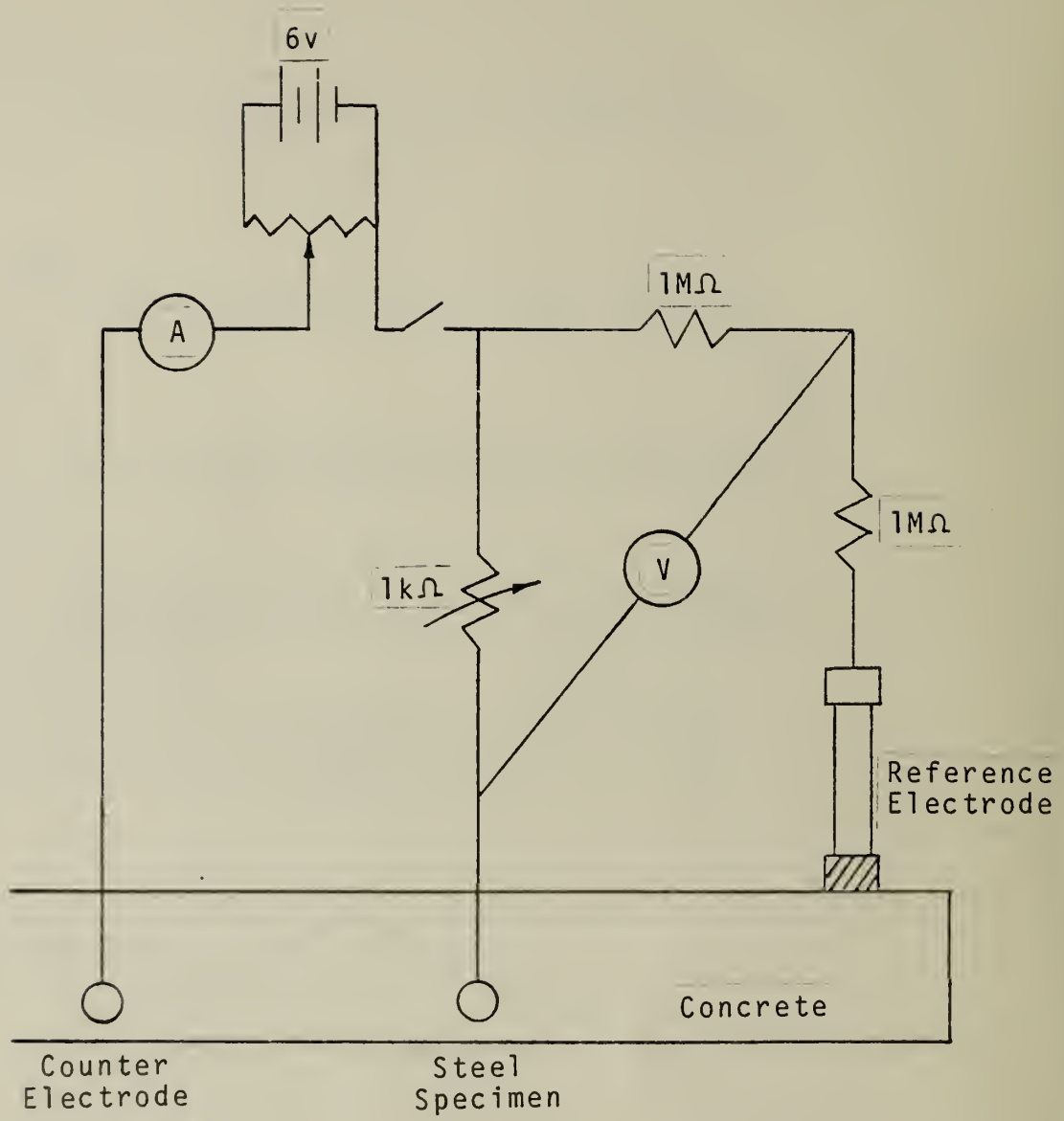

Figure 2. A Simplified Form Of The Circuit Used For Polarization Studies In Concrete

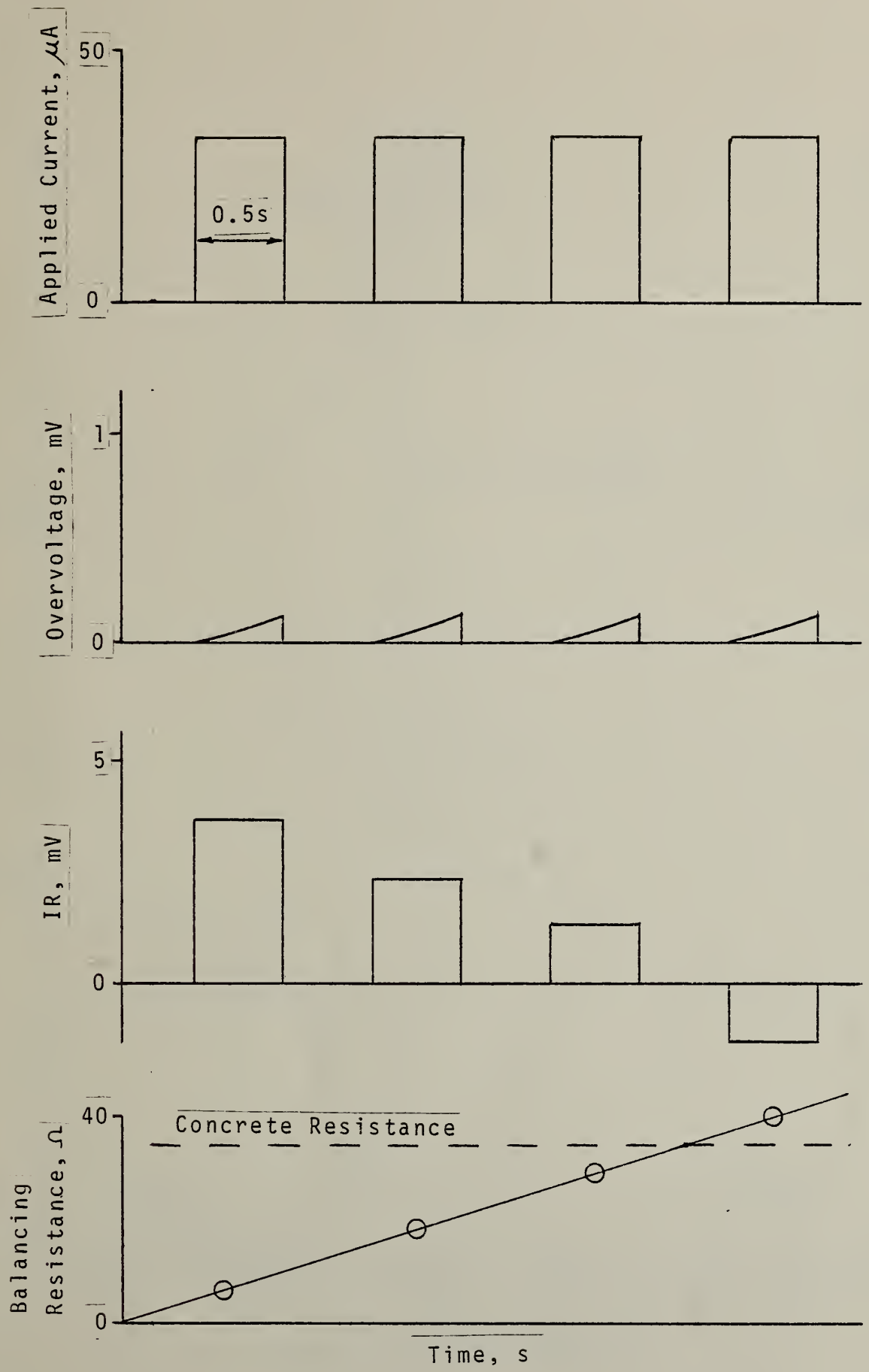

Figure 3. Idealized Response Of Polarization Circuit When Compensating For IR

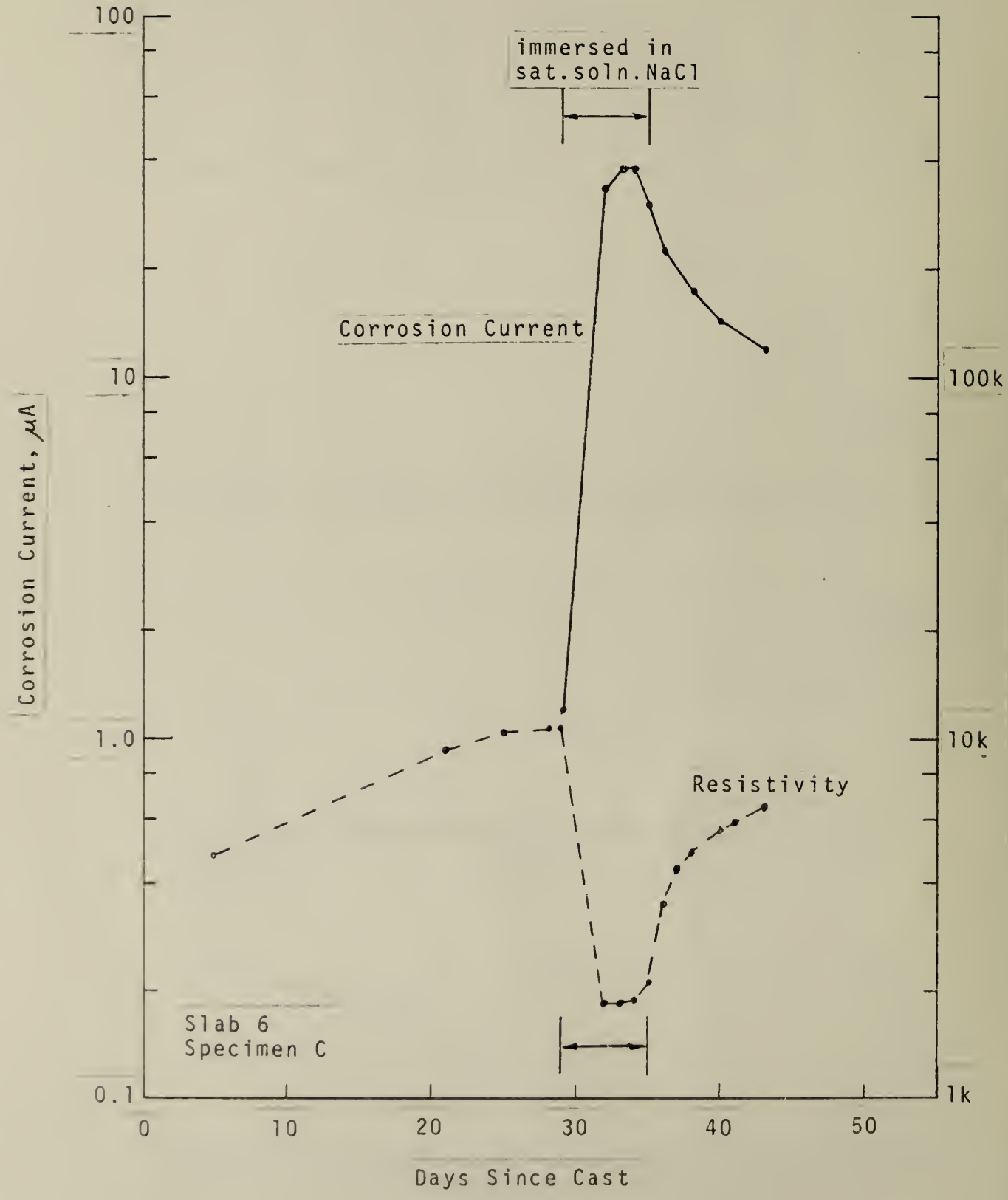

Figure 4. The Effect Of Immersion On The Corrosion Current Of Steel And The Resistivity Of Concrete

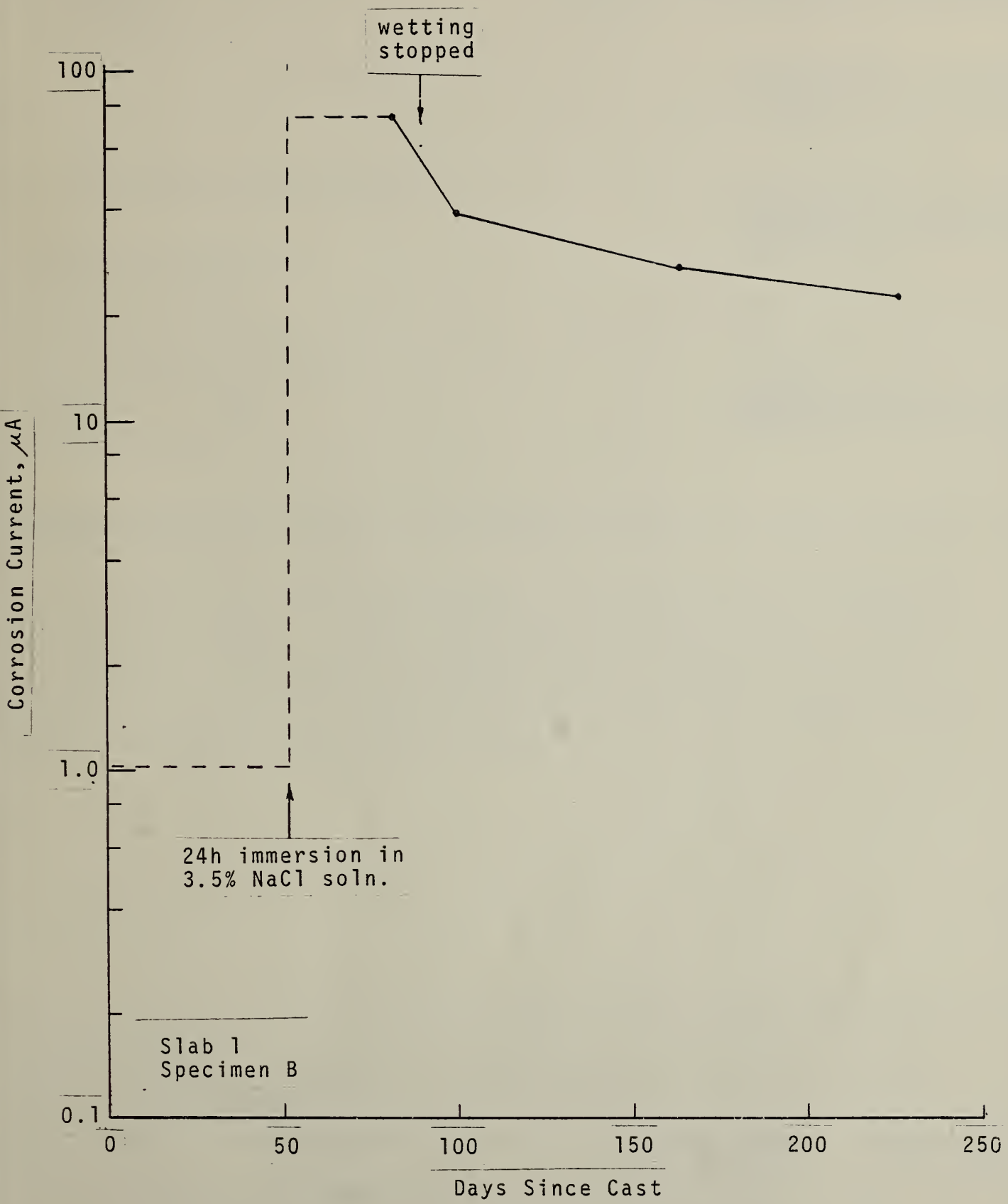

Figure 5. The Effect Of Immersion And Daily Wetting On The Corrosion Current Of Steel In Concrete

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The progress on a research program directed at developing a nondestructive method for measuring the corrosion of steel in concrete as related to bridge deck deterioration is reported. Several polarization techniques for measuring the corrosion rate of steel in concrete are correlated to actual weight loss measured gravimetrically. The design of a prototype automated minicomputer system for measuring the corrosion of steel in concrete is also described. Included are the results of a laboratory basic study on the effect of pH, Cl^-, O_2, and moisture on initiating and maintaining corrosion in mortar.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Bridge deck corrosion; corrosion in concrete; corrosion of steel; polarization technique; rebar corrosion

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